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(54) MANUFACTURE OF VINYL-SILANOL COPOLYMER DISPERSIONS

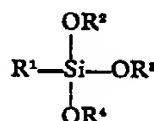
(71) We, WACKER-CHEMIE G.M.B.H., a body corporate organized according to the laws of the Federal Republic of Germany, of Prinzregentenstrasse 22, 8 München 22, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the manufacture of vinyl polymer dispersions, and also relates to the resulting polymers.

Aqueous dispersions of vinyl polymers are used in various ways as binders for adhesives, paints, and plastic-based pasters, and also as coating materials. The adhesion of these dispersions to mineral substrates, such as brickwork, concrete, glass and ceramics, is, however, not always satisfactory. In particular, when wet, the adhesion of the dispersion film to these materials extensively used in the building field declines, and frequently a complete detachment of the plastics dispersion layer occurs.

The present invention now provides a process for the manufacture of stable coagulate-free aqueous vinyl polymer dispersions having an improved adhesion. In this process (i) (a) one or more monomers selected from vinyl esters of carboxylic acids having from 2 to 18 carbon atoms, acrylic acid esters of alcohols having from 1 to 18 carbon atoms, and methacrylic acid esters of alcohols having from 1 to 18 carbon atoms, and optionally up to 25% by weight (relative to the total weight of component (i)) of one or more other singly-olefinically-unsaturated water-insoluble monomers, or (b) a mixture of styrene and

up to 40% by weight (relative to the mixture) of butadiene, is copolymerised with (ii) from 0.3 to 5% by weight (relative to the total weight of component (i)) of a silicon compound of the general formula



in which R¹ denotes an α-olefinically-unsaturated organic radical, and each of R², R³, and R⁴, which may be identical or different, denotes a hydrogen atom, an acyl radical, or a primary or secondary, unsubstituted or alkoxy-substituted alkyl radical, with the proviso that not more than two of R², R³, and R⁴ denote hydrogen atoms. Polymerisation is carried out at a temperature within the range of from -15 to +100° C., preferably from 20 to 90° C., in an aqueous phase, and in the presence of a water-soluble free-radical initiator and an emulsifier and/or protective colloid.

It is an important feature of this process that the silicon compound be metered in during the course of the polymerisation, that is to say that the silicon compound is added continuously to the polymerisation mixture during the course of the polymerisation rather than all being mixed in with the other monomers prior to or at the start of the polymerisation. This is necessary for the silicon monomer to become properly copolymerised with the other monomers, so as to give a coagulate-free dispersion. It is found that if all the silicon monomer is introduced initially into the polymerisation mixture, the resulting

dispersions contain appreciable amounts of coagulate and do not show an improved adhesion as shown by the dispersions produced according to the invention. The actual method used for metering in the silicon monomer is not critical, but usually it is metered in at the same rate as it is consumed. The course of the polymerisation can be followed in known manner, for example, by determination of the solids content or of the monomer content.

The silicon monomers used in the present process are of the general formula given above. These are hydrolysable compounds. During the polymerisation a large proportion of the alkoxy and acyloxy groups in the silicon monomer are hydrolysed, but particularly when there are three such groups in the monomer they are not necessarily all hydrolysed. The silicon compounds mainly used are those in which R^1 denotes an ω -unsaturated alkenyl radical having up to 10 carbon atoms, preferably up to 4 carbon atoms, or the radical of an ω -unsaturated carboxylic acid ester of a carboxylic acid having up to 4 carbon atoms and an alcohol having up to 6 carbon atoms; and each of R^2 , R^3 , and R^4 , which may be identical or different, denotes a hydrogen atom, a primary or secondary unsubstituted alkyl radical having up to 10 carbon atoms, preferably up to 4 carbon atoms, or an alkyl radical having up to 4 carbon atoms substituted by an alkoxy group, which preferably has up to 3 carbon atoms, or an acyl radical having up to 6 carbon atoms, preferably up to 3 carbon atoms. Examples of such compounds are vinyltrimethoxysilane, vinyltriethoxysilane, vinyl-diethoxysilanol, vinyl-ethoxysilanediol, vinyl-di(methoxy-methoxy)-silanol, allyltriethoxysilane, vinyltripropoxysilane, vinyltriisopropoxysilane, vinyltributoxysilane, vinyltriacetoxysilane, vinyltri(methoxymethoxy)-silane (vinyltrimethylglycolsilane), γ -methacryloxypropyltri(methoxy-methoxy)-silane (γ -methacryloxypropyltrimethylglycolsilane), γ -methacryloxypropyltriethoxysilane, and γ -acryloxypropyltriethoxysilane.

Vinyl esters that can be used as monomers in the present process are those of straight-chain and branched-chain carboxylic acids having 2 to 18 carbon atoms, preferably 2 to 12 carbon atoms; for example, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate, vinyl-2-ethylhexoate, vinyl isononate, vinyl stearate, vinyl laurate, and the vinyl ester of Versatic acid (Trade Mark). Mixtures of various vinyl esters can be used. In addition to the vinyl esters, up to a total of 25% by weight of one or more other water-insoluble singly-olefinically-unsaturated monomers can be copolymerised; for example vinyl and vinylidene halides, *e.g.* vinyl chloride, vinylidene chloride, vinyl fluoride, and vinylidene fluoride; olefins, preferably with 2 to 4 carbon atoms, *e.g.* ethylene, propylene, and

isobutylene; monoesters and diesters of unsaturated carboxylic acids with alcohols having up to 18 carbon atoms, *e.g.* methacrylic or acrylic acid esters, crotonic acid esters, maleic acid esters, fumaric acid esters, and itaconic acid esters. Preferably, ethylene is copolymerised, at a pressure of from 1 to 100 atmospheres gauge.

It is furthermore possible conjointly to use amounts of up to 10% by weight (relative to the total weight of water-insoluble monomers, that is of component (i)) of monomers with multiple olefinic unsaturation, for example, triallyl cyanurate, divinyl maleate, divinyl adipate, and vinyl crotonate, and/or of water-soluble monomers, for example, methacrylic acid, acrylic acid, maleic acid, fumaric acid, itaconic acid, the amides of these acids, vinylsulphonic acid and its alkali metal salts, and N-methylol acrylamide or methacrylamide.

Acrylic acid esters and methacrylic acid esters can also be polymerised according to the present process. These can be polymerised either alone (apart from the silicon monomer), or they can be copolymerised with the vinyl esters, or they can be copolymerised with up to 25% by weight of other water-soluble olefinically-unsaturated monomers as described above. The acrylic and methacrylic esters used are those with alcohols having up to 18 carbon atoms, for example, ethyl, propyl, butyl, or hexyl acrylate or methacrylate.

Mixtures of styrene and up to 40% by weight of butadiene can also be copolymerised according to the present process.

The dispersing agents used in the polymerisation mixture can be any of the emulsifiers and protective colloids usually used in emulsion polymerisation. It is possible to use protective colloids alone, emulsifiers alone, or mixtures of emulsifiers and protective colloids. As examples of protective colloids there may be mentioned polyvinyl alcohol, partly acetylated polyvinyl alcohol, water-soluble cellulose derivatives (*e.g.* hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, and carboxymethylcellulose), water-soluble starch ethers, polyacrylic acid, water-soluble polyacrylic acid copolymers with acrylamide and/or alkyl esters, and poly-N-vinyl compounds of open-chain or cyclic carboxylic acid amides.

As emulsifiers it is possible to use anionic, cationic, or non-ionic emulsifiers. Suitable anionic emulsifiers are, for example, alkylsulphonates, alkarylsulphonates, alkyl sulphates, sulphates of hydroxyalkanols, alkyl-disulphonates, alkaryldisulphonates, sulphonated fatty acids, sulphates and phosphates of alkyl- and alkarylpolylethoxy-alkanols, and sulphosuccinic acid esters. Examples of cationic emulsifiers which can be used are alkylammonium, alkylphosphonium, and alkylsulphonium salts. Examples of suitable non-ionic emulsifiers are addition products of 5 to 50 moles

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of ethylene oxide and/or propylene oxide per mole of straight-chain and branched-chain alkanols having 6 to 22 carbon atoms, alkyl-phenols, carboxylic acids, carboxylic acid amides, or primary and secondary amines; as well as block copolymers of propylene oxide with ethylene oxide.

Polymerisation is carried out in the presence of a water-soluble free-radical initiator, as customarily used in emulsion polymerisation. Examples of such initiators are hydrogen peroxide, sodium persulphate, potassium persulphate, ammonium persulphate, and tert-butyl hydroperoxide. They can be used by themselves or together with reducing agents as redox catalyst systems, suitable reducing agents being, for example, sodium formaldehyde-sulphoxylate, iron-II salts, sodium dithionite, sodium bisulphite, sodium sulphite, and sodium thiosulphate. The redox catalyst system described in German Patent Specification No. 1,133,130 and in German Auslegeschrift No. 1,745,567, which consists of a noble metal of group VIII of the Mendeleef Periodic System, an inorganic or organic peroxide, hydrogen as the reducing agent, and optionally a heavy metal ion, is also suitable.

The polymerisation mixture can also contain customary buffer salts, for example, alkali acetates, alkali carbonates, and alkali phosphates; and polymerisation regulators, such as mercaptans, aldehydes, chloroform, methylene chloride, and trichloroethylene.

Polymerisation is carried out at a temperature within the range of from -15 to $+100^{\circ}\text{C}$., preferably from $+20$ to $+90^{\circ}\text{C}$. If temperatures below 0°C . are used, it is necessary to add an anti-freeze agent, for example, methanol or glycol. The pH of the aqueous phase during polymerisation is generally weakly acid, preferably within the pH range of from 4 to 7. The process is generally carried out in pressure autoclaves which can be cooled with water and are equipped with stirring devices and metering devices.

The monomers (apart from the silicon monomers) either can be wholly introduced into the aqueous phase at the beginning of the polymerisation or can be wholly or partially metered in during the course of the polymerisation. Likewise the initiator, and, where appropriate, the reducing agent (which is used in the customary amounts of preferably from 0.01 to 1% by weight relative to the total weight of monomers), can be either initially introduced into the polymerisation mixture or can be metered in during the polymerisation.

The dispersions manufactured in accordance with the invention are free from coagulates and possess as good a stability to ageing and as good a mechanical stability as corresponding dispersions manufactured without organic silicon compounds. They contain from 0.3 to

5% by weight, relative to the polymer, of silanol units copolymerised in the polymer chain. They are distinguished from corresponding dispersions manufactured without organic silicon compounds by considerably improved adhesion towards a variety of mineral substrates, in the wet and dry states.

The adhesion can be measured simply by means of the following test procedure. The test substrate, for example glass or asbestos cement sheet strips 4 cm wide, is coated with dispersion and a linen strip is embedded in the dispersion whilst it is still moist and is fixed by again coating it with dispersion. After drying the test specimen in air for three days, the peel resistance at an angle of 180° is measured. For the wet adhesion, the dried test specimen is stored in water for 3 days before measurement and the peel resistance is measured on the wet test specimen.

The vinyl ester, acrylic ester and methacrylic ester homopolymers and copolymers and the butadiene-styrene copolymers, all of which contain copolymerised silanol units, can advantageously be used as polymeric binders for coating agents in buildings. Other uses are, for example, for coating glass fibres and as sealing agents.

Surprisingly, the uses of the polymer dispersions containing silanol units results in a greatly improved wet adhesion of the coating agents. This is of decisive importance especially in the case of substrates of glass, ceramic and glazed material. Furthermore it is found that the coating materials hardly swell, and only slightly soften, in the presence of water. A further advantage is that the coating agents have very good adhesion characteristics to foamed glass-building bricks. Hitherto, the use of these fire-resistant building materials was restricted for aesthetic reasons since customary coating agents showed inadequate adhesion and hence a coating which fulfilled the aesthetic requirements was not possible.

For the purposes of this specification, coating agents in buildings means all agents which are employed in the building industry in order to protect, beautify, or seal buildings or carry out similar processes. In particular, the polymers containing silanol units can be used as polymeric binders for the manufacture of emulsion paints and of plastics-based plasters.

Emulsion paints containing the polymer of the invention will generally comprise

- (a) 5 to 35 per cent by weight of the polymer containing silanol groups;
- (b) 5 to 35 per cent by weight of water;
- (c) 5 to 55 per cent by weight of filler; and
- (d) 5 to 30 per cent by weight of pigment.

Examples of fillers which can be employed are quartz flour, fine quartz sand, kaolin, highly disperse silica, feldspar, baryte, gypsum, calcium carbonate, chalk, dolomite and talc.

Titanium dioxide, zinc oxide and zinc sulphide may be mentioned as examples of pigments.

5 If desired, wetting agents, in amounts of 0.2 to 0.6% by weight relative to fillers, can be added to the paints. Possible wetting agents are anionic and non-ionic wetting agents. In most cases, polyphosphates, for example, sodium hexametaphosphate, naphthalenesulphonates, ammonium polyacrylates and sodium polyacrylates, are employed as wetting agents.

10 Further auxiliaries that can be used in the paints and thickeners. Organic thickeners are preferably employed in amounts of 0.01 to 1% by weight relative to the total paint. Examples of such thickeners are cellulose derivatives, alginates, starch and starch derivatives, and also polyacrylic acid. Inorganic thickeners may be used in amounts of 0.05 to 2% by weight relative to the total paint; bentonites or hectorite are preferably used.

20 Frequently, fungicides are also added as a preservative to the paints. They are employed in amounts of 0.01 to 2% by weight relative to the total paint. Examples of such fungicides are phenol and cresol derivatives, and organo-mercury and organo-tin compounds.

25 It is also possible to add anti-foaming agents, for example, silicone oils, alcohols and hydrocarbon in amounts of 0.1 to 0.5 per cent by weight relative to total paint; solubilising auxiliaries and film-forming auxiliaries, for example, glycol acetate and polyhydric alcohols, in amounts of 0.1 to 5 per cent by weight relative to total paint; anti-freeze agents, for example, methanol and glycol, in amounts of 1 to 5 per cent by weight relative to total paint; and dyestuffs, for example organic coloured pigments.

30 Plastics-based plasters consist of polymeric binders, coarse fillers and water. The ratios of the quantities of the individual constituents can vary very widely depending on the intended end use. At least 6% by weight of polymeric binders are present; the amount of filler and binder together is at most 90% by weight. The remainder consists of water.

45 As coarse-grained fillers it is possible to employ any granular material which possesses sufficient resistance to weathering. Examples of such materials are plastics granules, quartz fragments and stone materials. Their particle size is frequently between 0.2 and 5 mm. In some cases even larger particles are employed.

50 Possible auxiliaries may be wetting agents, anti-freeze agents, fungicides and dyestuffs. As auxiliaries, the compounds mentioned hereinbefore in connexion with emulsion paints may, for example, be employed.

60 The manufacture of the coating agents for building applications is carried out in accordance with the generally known processes, wherein homogeneous compositions are produced by thoroughly mixing the individual

constituents. The dispersions used according to the invention behave like corresponding dispersions without silanol groups when manufacturing the coating agents for buildings, so that tried formulations do not have to be modified as a result of the use of the dispersions according to the invention. It is also possible to employ appropriate dispersion powders.

A further advantageous use of the dispersions containing silanol groups is their use in structural adhesives. These comprise, for example,

- (a) 5 to 35% by weight, preferably 10 to 20% by weight, of a polymeric binder from a dispersion according to the invention;
- (b) 20 to 80% by weight, preferably 40 to 70% by weight, of filler; and
- (c) 15 to 45% by weight, preferably 20 to 40% by weight, of water

and, optionally, a wetting agent.

These structural adhesives are distinguished by excellent wet adhesion. In particular, it is surprising that very good adhesion in the wet state is achieved on glass, ceramics and glazed material. This also opens up new fields of use for structural adhesives.

The structural adhesives are produced by simply mixing the requisite constituents together. The polymeric binder is in most cases employed in the form of the aqueous dispersion but can be used in the form of a dispersion powder. Frequently, the liquid constituents are first mixed and the pulverulent substances then stirred in.

Water is present in the structural adhesive in an amount of from 15 to 45%, preferably 20 to 40%, by weight. This amount includes the water in the dispersion, when the polymeric binder is added as dispersion.

Examples of fillers which can be employed are quartz powder, fine quartz sand, kaolin, highly disperse silica, feldspar, baryte, gypsum, calcium carbonate, chalk, dolomite and talc.

If desired, wetting agents, fungicides and thickeners may be added to the structural adhesives in the same amounts as they are used in emulsion paints. Examples of wetting agents and fungicides and thickeners that can be used are as described hereinbefore in connexion with emulsion paints.

The structural adhesives according to the invention can be employed for gluing the most diverse materials. It is merely necessary that either the substrate or the material to be glued should be absorbent. Examples of inorganic materials are ceramic, stoneware and glass tiles, glass building bricks, glass, ceramic and stoneware mosaics, asbestos cement sheet and slag wool sheets. Organic materials are, for example, polystyrene foam, polystyrene and polyvinyl chloride sheets or tiles and poly-

urethane foam or polyester tiles. Possible absorbent substrates are, for example, concrete and mortar. A further field of use is to glue bricks together to give brick walls.

- 5 The water resistance of the adhesives is so good that they can even be employed for gluing coating materials in swimming pools.

The following Examples illustrate the invention.

Example 1.

- 10 A mixture of 5 g of sodium lauryl-sulphate, 35 g of nonylphenol-polyglycol-ether with 20 ethylene oxide units, 50 g of hydroxyethyl-cellulose of viscosity 300 cP in a 2% strength aqueous solution and 15 g of t-butyl hydroperoxide in 3.2 litres of water are initially introduced into a 10 litre stirred apparatus equipped with heating and cooling device, stirrer, reflux condenser and means for metering-in and for sampling, 700 g of vinyl acetate are then added and the polymerisation is started by adding a solution of 7 g of sodium formaldehyde-sulphoxylate and 4 g of sodium bicarbonate in 300 ml of water over the course of 3 hours. When the polymerisation commences, the addition, spread over 2 hours, of a solution of 35 g of tris(methoxy-methoxy)-vinylsilane in 500 g of vinyl acetate is started. As soon as the internal temperature has reached 70° C., a further 2300 g of vinyl acetate are metered in over the course of 1.5 hours and the internal temperature is kept at 70 to 75° C. After a further 30 minutes' reaction, the dispersion is warmed to 95° C. for 30 minutes and then cooled. A stable, coagulate-free dispersion having a residual vinyl acetate content of 0.20% is obtained. A film cast on a glass plate, which is dipped into water after drying can only be detached with mechanical force from the glass plate even after several days storage in water. The dry peel strength on glass is 7.0 kp/4 cm and the wet peel strength after three days' storage in water is 2.5 kp/4 cm.

Example 2 (comparison).

- 45 The procedure of Example 1 is followed but no tris(methoxy - methoxy)vinylsilane is metered in. A stable, coagulate-free dispersion with 0.15% residual vinyl acetate content is obtained. A film cast on a glass plate and dried swells and detaches from the glass plate after a short period of storage in water. The dry peel strength on glass is 0.9 kp/4 cm and the wet peel strength is zero.

Example 3 (comparison).

- 55 The procedure of Example 1 is followed but instead of metering-in the 35 g of tris(methoxy-methoxy)vinylsilane, it is initially introduced, dissolved in the first vinyl acetate addition of 700 g. The dispersion coagulates during polymerisation.

Example 4.

The procedure in Example 1 is followed but instead of 35 g of tris(methoxy-methoxy)-vinylsilane, 35 g of bis(methoxy-methoxy)-vinylsilanol is metered in. The dry peel strength of the dispersion film on glass is 6.0 kp/4 cm.

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Example 5.

A solution of 20 g of sodium alkylsulphonate (Mersolat K 30; Trade Mark), 75 g of nonylphenol-polyglycol-ether containing 23 ethylene oxide units, 10 g of sodium vinylsulphonate, 40 g of acrylic acid, 60 g of acrylamide and 5 g of potassium persulphate in 3.0 kg of water are initially introduced into a stirred apparatus as described in Example 1, a mixture of 500 g of vinyl acetate and 220 g of 2-ethylhexoic-acid vinyl ester is added and the whole is warmed whilst stirring. As soon as the reflux temperature is reached, metering-in of a solution of 70 g of tris(methoxy - methoxy)vinylsilane in 430 g of vinyl acetate is started. The solution is metered in at a speed such that 170 g are metered in during the first hour and then 100 g are metered in per hour. As soon as the internal temperature has reached 72° C., the following further metering-in is commenced:

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- 1) a mixture of 1670 g of vinyl acetate and 780 g of 2-ethylhexoic-acid vinyl ester, at a rate of 600 g per hour.
- 2) a solution of 10 g of sodium vinylsulphonate and 4 g of potassium persulphate in 0.7 kg of water at a rate of 250 g per hour.

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After completion of the addition of the monomer, the temperature is kept at 70 to 75° C. for one hour and is then raised to 95° C. for half an hour. After cooling, a stable, coagulate-free dispersion is obtained, of which the film cannot, without destruction, be detached from glass even after several days' storage in water.

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Example 6.

A solution of 4 g of sodium alkylsulphonate (Mersolat K 30—Trade Mark); 100 g of nonylphenol-polyglycol-ether with 30 ethylene oxide units, 20 g of vinyl sulphonate, 35 g of polyvinyl alcohol of saponification number 100 and 10 g of sodium formaldehyde-sulphoxylate in 3.3 litres of water are initially introduced into a stirred apparatus as described in Example 1, 800 g of vinyl propionate are added and the mixture is warmed to 55° C. whilst stirring. The polymerisation is started by the addition, spread over 3 hours, of 5 g of t-butyl hydroperoxide in a solution of 300 ml of water and 200 ml of methanol. When the polymerisation commences, the addition, spread over 3 hours, of 70 g of trimethoxyallylsilane in 500

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ml of vinyl propionate is started. 30 minutes after the start of polymerisation, 2.8 litres of vinyl propionate are metered in over the course of 2.3 hours, as a further stream. After completion of the addition of monomer, the polymerisation temperature is kept at 55° C. for a further hour and is subsequently raised to 80° C. for one hour. After cooling, a stable dispersion is obtained, of which the film adheres well to glass even when wet.

Example 7.

The procedure in Example 6 is followed but instead of vinyl propionate a mixture of 76% by weight of vinyl acetate and 23% by weight of butyl acrylate and 1% by weight of acrylic acid is used. The film of the stable dispersion has a wet peel strength of 2 kp/4 cm on glass.

Example 8.

A solution of 300 g of polyvinyl alcohol of saponification number 140 in 5 litres of water is initially introduced into a 16 litre stirred autoclave with means of metering-in and sampling and a heating and cooling device, and is freed of oxygen. 4.7 kg of vinyl acetate and 10 ml of an 0.1% strength palladium sol are added and the mixture is warmed to 40° C. whilst stirring. 36 atmospheres gauge of ethylene and 3 atmospheres gauge of hydrogen are then injected. The polymerisation is catalysed by the continuous metering-in of 80 g of potassium persulphate in 1 litre of water. The potassium persulphate solution is metered in over the course of three and a half hours in the amount required for utilisation of the cooling capacity at all times. The reaction temperature is kept at 40° C. and consumed ethylene is replaced. Simultaneously with the commencement of polymerisation, the metering-in of a solution of 75 g of triethoxyvinylsilane in 300 g of vinyl acetate is started. Of this solution, 40 g are metered in during the first half hour and thereafter 150 g are metered in per hour. Four and a half hours after the start of the polymerisation the mixture is cooled and excess ethylene is removed by releasing the pressure and applying a slight vacuum. A stable, coagulate-free dispersion, in which the copolymer contains 16% by weight of ethylene, is obtained, of which a film adheres excellently to glass and other mineral substances.

Example 9 (comparison).

A batch manufactured analogously to Example 8 but with the triethoxyvinylsilane being introduced at the start of the polymerisation coagulates during polymerisation.

Example 10.

A solution of 260 g of polyvinyl alcohol of saponification number 140, 100 g of isotridecyl alcohol adduct with 15 ethylene glycol

units, 9 g of Mersolat K 30 (Trade Mark) and 15 g of sodium sulphite in 5.5 litres of water is initially introduced into an apparatus as described in Example 8 and freed of atmospheric oxygen by flushing with nitrogen. 1 kg of vinyl acetate are then added, the mixture is warmed to 50° C. and ethylene is injected up to a pressure of 38 atmospheres gauge. The polymerisation is started by metering in 1 g of tert-butyl hydroperoxide in 50 g of vinyl acetate and is continued by constant metering-in of a solution of 5 g of tert-butyl hydroperoxide in 300 g of water and 300 g of methanol, with a speed of addition of 50 g/hour. At the start of the polymerisation, the metering-in of 75 g of tris(methoxy-methoxy)vinylsilane dissolved in 525 g of vinyl acetate is also started. Of this solution, 100 g are metered in during the first half hour and then 100 g per hour are metered in continuously. Fifteen minutes after the start of the polymerisation, the uniform metering-in of 3,500 g of vinyl acetate at 800 g per hour is begun. The reaction temperature is kept at 50° C. The ethylene pressure is kept at 38 atmospheres gauge for 4 hours. After a further three hours' polymerisation the mixture is cooled and the remaining ethylene is removed. A stable coagulate-free dispersion, in which the copolymer contains 18% by weight of ethylene, is obtained, the film of which on glass possesses a wet peel strength of 2.0 kp/4 cm and on asbestos cement a wet peel strength of 3.0 kp/4 cm. A comparison dispersion which was manufactured in exactly the same way except without the silane comonomer, gives wet peel strengths of 0 kp/4 cm on glass and of 0.2 kp/4 cm on asbestos cement.

Example 11.

An initially introduced solution, as described in Example 10, is flushed with nitrogen, 1 kg of vinyl acetate is then added, the mixture is warmed to 50° C. and ethylene is injected up to a pressure of 33 atmospheres gauge. The polymerisation is started by metering in 1 g of tert-butyl hydroperoxide in 50 g of vinyl acetate and is continued by constant metering-in of a solution of 5 g of tert-butyl hydroperoxide in 200 g of water and 300 g of methanol, at a speed of addition of 50 g/hour, at 50° C. When the polymerisation commences, the metering-in of a homogeneous solution of 75 g of tris(methoxy-methoxy)vinylsilane in 525 ml of water is also started. 100 g of this solution are metered in during the first half hour and then 100 g/hour are metered in continuously. The aqueous solution of the tris(methoxy-methoxy)vinylsilane is freshly prepared before use by dropwise addition to water, with vigorous stirring, and further stirring until a homogeneous mixture has formed. 20 minutes after the commencement of polymerisation, the metering-in of 4.0 kg of vinyl acetate in a stream of 800 g per hour is

started and after completion of the addition polymerisation is continued for 3 hours. A stable, coagulate-free dispersion, in which the copolymer contains 14% by weight of ethylene, is obtained, of which a film shows a wet peel strength on glass of 3 kp/4 cm and on asbestos cement of 2.9 kp/4 cm.

Example 12 (comparison).

The procedure in Example 11 is followed except that the aqueous tris(methoxy-methoxy)vinylsilane solution is all introduced at the start of the polymerisation. An unusable dispersion which contains a great deal of coagulate is obtained, whilst the polymerisation is noticeably slowed down.

Example 13.

Wet Adhesion of Emulsion Paints

The following procedure was used to test the wet adhesion: glass plates 4 cm wide and 15 cm long were coated with the emulsion paints to be tested, using a wet film thickness of 300 μ , a glass fibre fabric (Mikrolit fabric 174 G) of size 4 \times 17 cm was placed on top and worked in with a roller in such a way that 2 cm overlapped at the narrow side of the glass plate, and the fabric was again coated with the emulsion paint to be tested, using a wet film thickness of 200 μ . After a

drying time of 7 days in standardised climatic conditions of 22°C./50% relative atmospheric humidity, a part of the glass plates were placed in water and left under water for 7 days. The adhesion was tested by clamping the coated glass fabric and the glass plate in a tensile test instrument and peeling off the coated glass fabric at an angle of 180°. The peel strength was measured on groups of 5 test specimens and the mean value was computed. The emulsion paints to be tested had a pigment concentration of 35 or 45 or 52.5% by volume, as is customary for external emulsion paints. The following separate pastes were used for the manufacture of the emulsion paints:

(a) Pigment paste of 1.52 kg of rutile titanium dioxide, 2.70 kg of barium sulphate, particle size up to maximally 5 μ , and 650 ml of a 1% strength solution of sodium hexametaphosphate.

(b) Dispersion mixture: the dispersion mixture consisted of 100 g of the plastics dispersion to be tested (50% by weight solids), 20 g of a 2% strength solution of a highly viscous hydroxyether-cellulose in water and 1 g of anti-foaming agent (mixture of higher alcohols and hydrocarbons). The ratios of the quantities of pigment paste and dispersion mixture for the individual pigment volume concentrations tested can be seen in Table I.

TABLE I

Pigment volume concentration, %	(a) Pigment paste g	(b) Dispersion mixture g
35	384	403
45	439	300
52.5	464	239

To supplement the experiments with glass, the same experiments were also carried out on fluosilicate-treated asbestos cement sheets of the same size. If the samples were stored dry and the peel strength was tested, the film broke, whilst if they were stored wet

and the peel strength was tested, separation took place at the film/substrate interface.

The following plastics dispersions, prepared as described below, were used (50% by weight solids content):

- A: Copolymer of approx. 82% by weight of vinyl acetate and 18% by weight of ethylene
 B: " " " 82% by weight of vinyl acetate and 18% by weight of ethylene+1.75% by weight of vinyl silanol (produced by hydrolysis of triethoxyvinylsilane during the polymerisation)

	C: Terpolymer from	25% by weight of vinyl chloride,	
		25% by weight of vinyl laurate and	
		50% by weight of vinylacetate	
5	D: " "	25% by weight of vinyl chloride,	
		25% by weight of vinyl laurate and	
		50% by weight of vinyl acetate+1.5%	
		by weight of vinylsilanol (pro-	
		duced from triethoxyvinylsilane	
		during the polymerisation).	
10	Dispersion B is prepared using the procedure of Example 8, except that an ethylene pressure of 40 atmospheres gauge is used, and 105 g of triethoxyvinylsilane, dissolved in 300 g of vinyl chloride are metered in. A stable, co-		
15	agulate-free copolymer dispersion with an ethylene content of 18% is obtained.		
	Dispersion A is prepared similarly but without the silane.		
	Dispersion D is prepared as follows:		
20	In a reaction vessel as described in Example 8, 4.6 kg of water, 100 g of hydroxyethylcellulose with a viscosity of 300 cP at 25° C., contained in 2% by weight aqueous solution, 70 g of a polyethylene glycol ether of lauryl alcohol with, on average, 10 ethylene oxide units per molecule, and 8 g of sodium salt of a mixture of secondary alkyl sulphonic acids having 10—16 C atoms, are dissolved,		
25	and freed from oxygen. Then a mixture of 2.5 kg vinyl acetate, 1.25 kg vinyl chloride, 1.25 kg vinyl laurate, and 10 g tertiary-butyl hydroperoxide is added. The contents heated, with stirring, to 65° C., then there is metered in at the rate of 80 cm ³ in the first half hour and 60 cm ³ per hour thereafter, a solution of 5 g of formaldehyde sodium sulfoxylate, 11 g sodium bicarbonate in 500 g of water. When polymerisation sets in, then 75 g of vinyltriethoxysilane, dissolved in 300 g vinyl acetate, is metered in over a period of 6 hours. After a further hour of postpolymerisation at 65° C., cooling is carried out. A stable, co-		
	agulate-free dispersion is obtained.		
	Dispersion C is prepared similarly but without any silane.		
	The results of the tests are shown in Table II.		

TABLE II

Plastics dispersion	Pigment volume concentration, %	Peel strength on glass after 7 days' storage under water, kp/4cm Mean value	Peel strength on asbestos cement after 7 days' storage under water, kp/4 cm Mean value
A	35	less than 0.1	1.3
	45	" " 0.1	1.25
	52.5	" " 0.1	1.0
B	35	1.8	2.1
	45	2.1	2.0
	52.5	2.1	2.1
C	35	less than 0.1	1.6
	45	" " 0.1	1.4
	52.5	" " 0.1	1.3
D	35	1.7	2.0
	45	1.9	2.1
	52.5	1.8	2.1

Example 14.

Softening of Plastics-based Plasters

A plastics-based plaster was manufactured in accordance with the following formulation:

- 5 150 kg of mica particle size 100 to 500 μ
 30 kg of dolomite of particle size approx. 30 μ
 30 kg of rutile titanium dioxide
 10 150 kg of barium sulphate, particle size up to 10 μ
 100 kg of quartz powder, particle size up to approx. 80 μ
 140 kg of quartz sand, particle size 0.1 to 0.4 mm
 15 140 kg of quartz sand, particle size 0.2 to 0.6 mm
 50 kg of round quartz sand, particle size 1.5 to 2 mm
 20 0.1 kg of sodium hexametaphosphate
 2.5 kg of organo-mercury fungicide
 2.5 kg of anti-foaming agent (mixture of higher alcohols and hydrocarbons)

31 kg of a 3% strength methylcellulose solution (1500 cP)
 170 kg of plastics dispersion.

25

This plaster was applied by means of a trowel to fluosilicate-treated asbestos cement sheets, and smoothed. The layer thickness was approx. 2 to 3 mm. The sheets were hardened for 7 days under standard climatic conditions (22° C./50% relative atmospheric humidity) and then stored under water. They were tested for softening according to DIN 53,153, using the Buchholz penetration test body, but the conversion calculation according to DIN was not carried out and instead merely the depth of penetration of the test body, in mm, was measured. The same plastics dispersions as in Example 13 were used. The test for softening was carried out after 5, 24, 48, 72 and 96 hours. The results are contained in Table III.

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TABLE III

Softening of Plastics-Based Plaster

Plastics dispersion	Depth of penetration of the test body, in mm					
	Before storage in water	After storage in water for				
		5 h	24 h	48 h	72 h	96 h
A	0.5	4	6	8	9	10
B	0.5	2	2	3	4	4
C	0	2	4	4	4	4
D	0	0	0	1	0	0
E	0	3	7	9	10	10
F	0	1	5	5	5	4

Example 15.

- 45 A foamed glass building brick was coated with each of the plastics-based plasters of the formulations according to Example 14. After a drying time of 7 days under standard climatic conditions (22° C./50%) the plastics-bound plasters were tested for their adhesion. After hardening, a part of the glass building bricks was stored under water for 7 days. It was found that all plastics-bound plasters which contained the dispersions according to the invention as binders could not be pulled off the glass building bricks whilst all plastics-based plasters which contained the unmodified dispersions as binders

could be peeled off the substrate without exerting force. A difference in the adhesion was also found in the case of the bricks which were stored dry.

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Example 16.

Structural adhesives were manufactured in accordance with the following formulation:

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- 100 parts of plastics dispersion
 5 parts of sodium hexametaphosphate, 10% strength in water
 150 parts of quartz powder, particle size up to 80 μ
 30 parts of kaolin.

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Six polymer dispersions of 50% by weight solids content as described in Example 13 were employed as the plastics dispersion.

- 5 These adhesives were applied by means of a saw-edged trowel to a series of concrete pavement slabs and after 5 minutes' exposure to air 5 × 5 cm ceramic tiles were embedded in it. After 7 days' drying in standard climatic conditions (22° C./50% relative atmospheric

humidity) the tensile strength was tested. After thorough drying, a part of each slab was stored for 7 days under water. In the course thereof, the adhesive layer becomes wet throughout. The tensile strength values obtained after the test are contained in the Table IV. If ceramic mosaic or glass mosaic is used instead of ceramic tiles, similar results are obtained.

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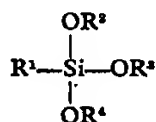
TABLE IV

Tensile Strength of Ceramic Tiles Glued on to Concrete Pavement Slabs

Plastics dispersion	Mean value of 4 measurements in kp/cm	
	Dry	After 7 days under water
A	5.4	1.6
B	6.3	1.8
C	5.1	0.8
D	5.6	2.7
E	5.9	1.5
F	5.7	3.1

WHAT WE CLAIM IS:—

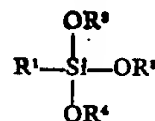
- 20 1. Process for manufacture of a polymer dispersion, which comprises copolymerising (i) one or more vinyl esters of carboxylic acids having from 2 to 18 carbon atoms, and optionally up to 25% by weight (relative to the total weight of component (i)) of one or more other singly-olefinically-unsaturated water-insoluble monomers, and (ii) from 0.3 to 5% by weight (relative to the total weight of component (i)) of a silicon compound of the general formula



- 35 in which R¹ denotes an ω-olefinically-unsaturated organic radical, and each of R², R³, and R⁴, which may be identical or different, denotes a hydrogen atom, an acyl radical, or a primary or secondary, unsubstituted or alkoxy-substituted, alkyl radical, with the proviso that not more than two of R², R³, and R⁴ denote hydrogen atoms, in an aqueous phase, and in the presence of a water-soluble free-radical initiator and an emulsifier and/or protective colloid, at a temperature within the

range of from -15 to +100°C., wherein the silicon compound is metered in during the course of the polymerisation.

2. Process for the manufacture of a polymer dispersion, which comprises copolymerising (i) (a) one or more monomers selected from vinyl esters of carboxylic acids having from 2 to 18 carbon atoms, acrylic acid esters of alcohols having from 1 to 18 carbon atoms, and methacrylic acid esters of alcohols having from 1 to 18 carbon atoms, and optionally up to 25% by weight (relative to the total weight of component (i)) of one or more other singly-olefinically-unsaturated water-insoluble monomers, or (b) a mixture of styrene and up to 40% by weight (relative to the mixture) of butadiene, and (ii) from 0.3 to 5% by weight (relative to the total weight of component (i)) of a silicon compound of the general formula



in which R¹ denotes an ω-olefinically-unsaturated organic radical, and each of R², R³, and R⁴, which may be identical or different,

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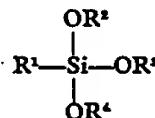
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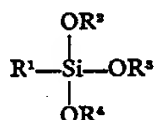
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- denotes a hydrogen atom, an acyl radical, or a primary or secondary, unsubstituted or alkoxy-substituted, alkyl radical, with the proviso that not more than two of R², R³, and R⁴ denote hydrogen atoms, in an aqueous phase, and in the presence of a water-soluble free-radical initiator and an emulsifier and/or protective colloid, at a temperature within the range of from -15 to +100° C., wherein the silicon compound is metered in during the course of the polymerisation.
3. Process as claimed in claim 1 or claim 2, wherein in the general formula R¹ denotes an ω-unsaturated alkenyl radical having up to 10 carbon atoms, or the radical of an ω-unsaturated carboxylic acid ester of a carboxylic acid having up to 4 carbon atoms and an alcohol having up to 6 carbon atoms; and each of R², R³, and R⁴, which may be identical or different, denotes a hydrogen atom, a primary or secondary alkyl radical having up to 10 carbon atoms, an alkoxy-substituted alkyl radical having up to 4 carbon atoms, or acyl radicals having up to 6 carbon atoms.
4. Process as claimed in claim 3, wherein R¹ denotes an ω-unsaturated alkenyl radical having up to 4 carbon atoms.
5. Process as claimed in claim 3 or claim 4, wherein at least one of R², R³, and R⁴ denotes an unsubstituted alkyl radical having up to 4 carbon atoms.
6. Process as claimed in any one of claims 3 to 5, wherein at least one of R², R³, and R⁴ denotes an alkoxy-substituted alkyl radical, the alkyl moiety having up to 4 carbon atoms and the alkoxy moiety having up to 3 carbon atoms.
7. Process as claimed in any one of claims 3 to 6, wherein at least one of R², R³, and R⁴ denotes an acyl radical having up to 3 carbon atoms.
8. Process as claimed in claim 1 or claim 2, wherein the silicon compound is vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriethoxysilanol, vinyltriethoxysilanediol, allyltriethoxysilane, vinyltripropoxysilane, vinyltriisopropoxysilane, vinyltributoxysilane, vinyltriacetoxysilane, vinyltri(methoxy - methoxy)silane, γ-methacryloxypropyltri(methoxymethoxy)silane, γ-methacryloxypropyltrimethoxysilane or γ-acryloxypropyltriethoxysilane.
9. Process as claimed in any one of claims 1 to 8, wherein the silicon compound is metered in at the rate at which it is consumed by the polymerisation.
10. Process as claimed in any one of claims 1 to 9, wherein polymerisation is carried out at a temperature within the range of from 20 to 90° C.
11. Process as claimed in any one of claims 1 to 10, wherein the vinyl ester is an ester of a carboxylic acid having 2 to 12 carbon atoms.
12. Process as claimed in any one of claims 1 to 11, wherein a vinyl ester is copolymerised with up to 25% by weight (relative to the total weight of component (i)) of one or more monomers selected from vinyl halides, vinylidene halides, olefins, and monoesters and diesters of unsaturated carboxylic acids with alcohols having up to 18 carbon atoms.
13. Process as claimed in claim 12, wherein a vinyl ester is copolymerised with ethylene at a pressure within the range of from 1 to 100 atmospheres gauge.
14. Process as claimed in any one of claims 1 to 11, wherein an acrylic acid ester and/or a methacrylic acid ester is copolymerised with a vinyl ester.
15. Process as claimed in any one of claims 1 to 10 and 14, wherein an acrylic acid ester and/or a methacrylic acid ester is copolymerised with up to 25% by weight (relative to the total weight of component (i)) of one or more monomers selected from vinyl halides, vinylidene halides, olefins, and monoesters and diesters of unsaturated carboxylic acids with alcohols having up to 18 carbon atoms.
16. Process as claimed in claim 15, wherein an acrylic acid ester and/or a methacrylic acid ester is copolymerised with ethylene at a pressure within the range of from 1 to 100 atmospheres gauge.
17. Process as claimed in any one of claims 1 to 16, wherein up to 10% by weight (relative to the total weight of component (i)) of one or more multiply-olefinically-unsaturated monomers and/or of one or more water-soluble monomers is copolymerised with the other monomers.
18. Process as claimed in any one of claims 1 to 17, wherein the pH of the aqueous polymerisation mixture is within the range of from 4 to 7.
19. Process as claimed in claim 1, carried out substantially as described in any one of Examples 1, 4 to 8, 10 and 11 herein.
20. Polymer dispersion manufactured by a process as claimed in claim 1.
21. Polymer dispersion manufactured by a process as claimed in any one of claims 2 to 19.
22. Copolymer comprising (i) units from one or more vinyl esters of carboxylic acids having from 2 to 18 carbon atoms, and optionally up to 25% by weight (relative to the total weight of component (i)) of units from one or more other singly-olefinically-unsaturated water-insoluble monomers; (ii) from 0.3 to 5% by weight (relative to the total weight of component (i)) of units from a silicon compound of the general formula



in which R¹ denotes an α -olefinically-unsaturated organic radical, and each of R², R³, and R⁴, which may be identical or different, denotes a hydrogen atom, an acyl radical, or a primary or secondary, unsubstituted or alkoxy-substituted, alkyl radical, with the provisos that not more than two of R², R³, and R⁴ denote hydrogen atoms, and that in the copolymer at least some of these units should contain silicon-bonded hydroxy groups; and optionally (iii) up to 10% by weight (relative to the total weight of component (i)) of units from one or more multiply-olefinically-unsaturated monomers and/or of one or more water-soluble monomers.

23. Copolymer consisting essentially of (i) (a) units from one or more monomers selected from vinyl esters of carboxylic acids having from 2 to 18 carbon atoms, acrylic acid esters of alcohols having from 1 to 18 carbon atoms, and methacrylic acid esters of alcohols having from 1 to 18 carbon atoms, and optionally up to 25% by weight (relative to the total weight of component (i)) of units from one or more other singly-olefinically-unsaturated water-insoluble monomers, or (b) units from styrene and up to 40% by weight of units from butadiene (relative to the total weight of styrene units and butadiene units); (ii) from 0.3 to 5% by weight (relative to the total weight of component (i)) of units from a silicon compound of the general formula



in which R¹ denotes an α -olefinically-unsaturated organic radical, and each of R², R³, and R⁴, which may be identical or different, denotes a hydrogen atom, an acyl radical, or a primary or secondary, unsubstituted or alkoxy-substituted, alkyl radical, with the provisos that not more than two of R², R³, and R⁴ denote hydrogen atoms, and that in the copolymer at least some of these units should contain silicon-bonded hydroxy groups; and optionally (iii) up to 10% by weight (relative to the total weight of component (i)) of units from one or more multiply-olefinically-unsaturated monomers and/or of one or more water-soluble monomers.

24. Coating agent for building purposes, containing, as a polymeric binder, a copolymer as claimed in claim 22 or claim 23.

25. Coating agent as claimed in claim 24, in the form of an emulsion paint.

26. Coating agent as claimed in claim 24, in the form of a structural adhesive. 55

27. Coating agent as claimed in claim 24, in the form of a plastics-based plaster.

28. Emulsion paint comprising

- (a) 5 to 35% by weight of a copolymer as claimed in claim 22 or claim 23; 60
- (b) 5 to 35% by weight of water;
- (c) 5 to 55% by weight of filler; and
- (d) 5 to 30% by weight of pigment.

29. Structural adhesive comprising 65

- (a) 5 to 35% by weight of a copolymer as claimed in claim 22 or claim 23;
- (b) 20 to 80% by weight of a filler; and
- (c) 15 to 45% by weight of water.

30. Structural adhesive comprising 70

- (a) 10 to 20% by weight of a copolymer as claimed in claim 22 or claim 23;
- (b) 40 to 70% by weight of filler; and
- (c) 20 to 40% by weight of water.

31. Plastics-based plaster comprising at least 6% by weight of a copolymer as claimed in claim 22 or claim 23, and a maximum of 90% by weight total filler and copolymer, the remainder being water. 75

32. Emulsion paint as claimed in claim 28, or structural adhesive as claimed in claim 29, or plastics-based plaster as claimed in claim 31, which also contains an anionic or non-ionic wetting agent in an amount of from 0.2 to 0.6% by weight relative to the filler. 80

33. Emulsion paint as claimed in claim 28, or structural adhesive as claimed in claim 29, which also contains an organic thickener in an amount of from 0.01 to 1% by weight relative to the total paint or adhesive, or an inorganic thickener in an amount of 0.05 to 2% relative to the total paint or adhesive. 85

34. Emulsion paint as claimed in claim 28, or structural adhesive as claimed in claim 29, or plastics-based plaster as claimed in claim 31, which also contains a fungicide in an amount of from 0.01 to 2% by weight relative to the total adhesive. 90

35. Emulsion paint as claimed in claim 28 substantially as described in Example 13 herein. 100

36. Plastics-based plaster as claimed in claim 31, substantially as described in Example 14 herein.

37. Structural adhesive as claimed in claim 29, substantially as described in Example 16 herein. 105

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